Real Time Observation of Nonlinear Coherent Phonon Dynamics in Single-Wall Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are π-electron, rod-shaped nanostructures with a distinct one-dimensional (1-D) character. The electronic structure, according to geometrical criteria, gives rise to metallic and semiconducting SWNTs. In semiconductors, medium-sized excitons (3–5 nm) are regarded as the fundamental excitation. As a consequence of exciton wavefunction localization and the 1-D character, electron-phonon coupling is expected to be substantial in SWNTs. The time domain observation of phonon dynamics allows direct measurement of excited state dynamics, vibrational dephasing and mode coupling.

Resonant sub-10-fs visible pulses were used to generate and detect coherent phonons in SWNT ensembles. We observed vibrational wavepacket dynamics for the radial breathing mode (RBM) and the longitudinal carbon-stretching mode (G), and in particular their anharmonic coupling. As shown in Fig. 1a, there is a clear oscillation in ΔT/T amplitude. The Fourier transform (FT) of the oscillatory component (Fig. 2a) shows a strong peak at 254 cm^{-1} (131 fs period), recognized as the RBM, associated with expansion and contraction of the tube cross section. Our observation corresponds to an ensemble of semiconducting SWNTs, with diameters of about 0.95 nm, all vibrating in phase.

We further used Los Alamos National Laboratory- (LANL)-developed quantum-chemical computational tool (a semiempirical Excited State Molecular Dynamics, ESMD) approach to understand the underlying dynamics. Calculations based on ESMD confirm that both the RBM and G modes have substantial coupling with the electronic transitions. The RBM and G-mode are both Raman-active Frank-Condon vibrations, i.e., their equilibrium positions change upon electronic excitation. Calculated dimensionless displacements from the ground state to the lowest optically active exciton state are 0.2 for the RBM and 0.4 for the G mode for the chiral (7,6) tube. However, tube-diameter modification in going from the ground to the first exciton state is not as simple as expected. In Fig. 3a, we display the change in tube radius *dr* with atom coordinate along tube Z axis calculated for the (7,6) tube shown

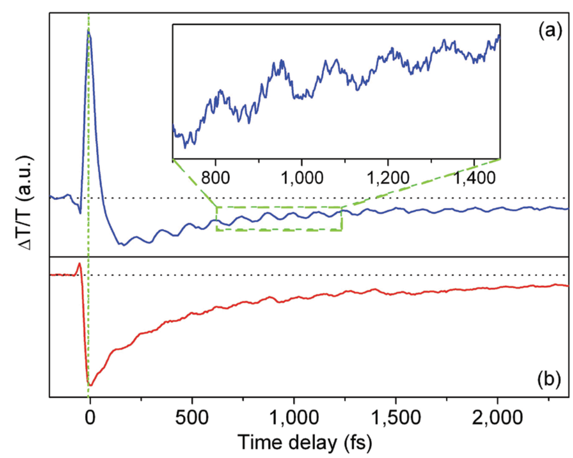

Fig. 1.
Fig. 1. Differential transmission (ΔT/T) dynamics of SWNTs excited and probed by a sub-10-fs visible pulse. Inset shows the high frequency modulation.

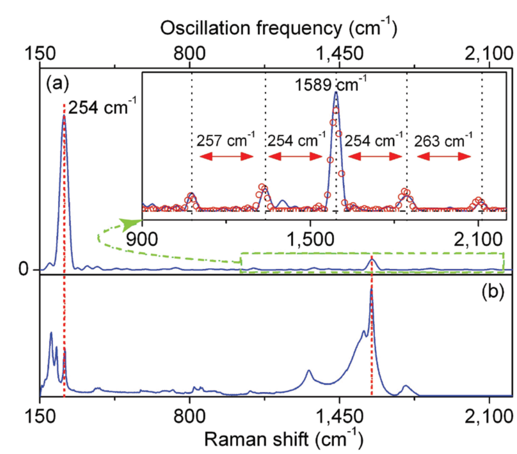

Fig. 2.
(a) FT power spectrum of time trace shown in the top. Inset: Solid line is the zoom of the FT power spectrum, showing side bands in the high frequency region. Regular spacing between the modes is shown by labels and double arrows. (b) CW Raman spectrum.

in the inset. Overall, relaxation of the photoexcitation results in an increase of the average diameter in the middle of the tube. Surprisingly, there is also a corrugation of the tube surface in the excited state, which clearly leads to coupling of radial and longitudinal modes.

Finally, to explore the anharmonic coupling between RBM and G-mode in the excited state, we ran molecular dynamics (MD) simulations. In the ground state, the trajectories (not shown) are perfectly harmonic. The situation is very different in the excited state. Fig. 3b shows the FT of a 1-ps trajectory. In addition to the fundamental RBM frequency, we observe a weak satellites component of the excited state G-mode frequency appearing due to linear mixing of the G and RBM in the excited state. This provides computational confirmation of anharmonic coupling between radial and longitudinal modes induced in the excited state.

In summary, this study shows that ultrashort light pulses can drive coherent atomic motion in SWNTs, in spite of the large inhomogeneous broadening. We have demonstrated the high selectivity of the mechanism. With such a technique, nonlinear MD can be observed. The exciton state modulates the phonon field introducing the nonlinearity, which manifests itself as vibrational coupling. Quantum-chemical dynamic computations show that upon excitation, the surface of the nanotubes corrugates, inducing a coupling between the radial and longitudinal modes, manifesting itself in the frequency modulation experimentally observed in the time domain.

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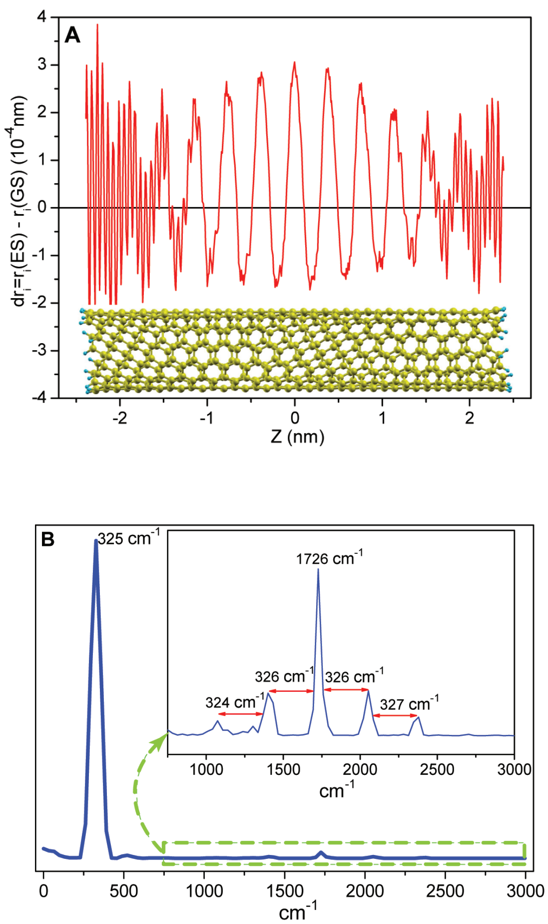

Fig. 3.
(a): Comparison of calculated excited and ground state optimal geometries. Modification of radius dr with carbon coordinate along the tube Z axis for the (7,6) SWNT shown in the inset; (b): FT power spectrum of the trajectory of RBM dimensionless displacement calculated using ESMD approach. Inset: Zoom-out of the FT power spectrum, showing side bands in the high frequency region, which proves experimentally observed vibrational coupling on the excited state.